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MEASUREMENTS OF IONS FORMED IN JET ENGINE EXHAUST PLUMES

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An atmospheric pressure chemical ionization mass spectrometer was modified to measure either ion or neutral effluents from a jet engine. The instrument was set up behind an F-15 aircraft at Eglin Air Force Base and measured the ions formed in both the positive and negative spectrum. Since the ion concentrations in the jet plume were quite small and measurement times relatively short, most of the measurements performed were of ions artificially produced in the exhaust using a corona ion source. The most obvious change in the ion spectrum after the jet engines were started was the dramatic increase in what appeared to be sulfuric acid. The spectra resulting from these measurements are shown and discussed.

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Introduction

The work proposed for the first year of this project was the adaptation of an ion sampling apparatus [1,2] to make possible measurements behind a jet engine. The modified apparatus was then to be taken into the field to perform preliminary measurements of actual engine exhaust. Both of these tasks have been successfully accomplished, and the latter has resulted in a substantial amount of very interesting new data which is still being analyzed.

The effort began with a visit to Hanscom AFB and a detailed discussion of the measurement environments and types of data that were needed. A new Teflon flow opposed drift tube (sample and ion separation tube)[2] was then fabricated and tested to withstand the relatively high exhaust gas temperatures incurred behind a jet engine. Next, a large insulated aluminum and wood container 8' x 4' x 6' high was constructed to house the instrument. This container served as both a shipping container and a protective housing, which allowed the ion measuring instrument's electronics and pumping system to operate in the hot jet exhaust plume being studied. The container also sheltered the apparatus from severe weather while on the runway. Once the instrument was started and fully enclosed in the container, it was designed to function independently under computer control and to require only electrical power and cooling air to complete its measurements.

Apart from a brief test just prior to shipping, the first real test of the instrument housed in the container was at Eglin AFB behind an F-15's engines. The Eglin measurements began on July 27 after two days of instrument setup and testing. Thunderstorms persisted throughout most of the day on July 27, so flights were held to a minimum and only one approximately nine-minute long engine run could be made available for measurement. The weather was more favorable the next two days, allowing for more measurements. Exhaust from two runs, approximately seven- and ten minutes long was measured on July 28. Measurements were also performed throughout 12- and 15-minute runs on July 29. Thus, a total of five sets of measurements were made, each including at least several jet exhaust spectra from F-15 engines and several background spectra. In addition, several data sets also included spectra with both a corona ion source turned on and off and, in one

case, two different distances behind the jet engines. The use of a corona ion source was necessitated by the lack of ions present in the jet exhaust. At the 75-170 foot distances behind the engines at which measurements were made, the ions generated by the engines appeared to be at concentrations comparable to ambient ion concentrations levels (~10^3 ions/cm^3). While the instrument being used to measure the ions in the jet exhaust is very similar to that previously used to measure natural ion spectra, the latter measurements are performed using integration times of one minute per mass as opposed to a fraction of a second per mass unit which was used for the brief engine measurements.

If one were to move closer to the engines, the ion concentrations might increase somewhat; however, the rise in ion concentration would probably not be more rapid than a 1/t functional dependence, where t is the engine to instrument exhaust transit time. The engine exhaust that was being measured was only from engines that were in the "idling" mode (with a few brief exceptions), and ion production could be below some threshold value. Thus, ion concentrations generated from an in-flight engine under normal operating conditions could be quite different. Even if engine-produced ion concentrations had been much higher than those observed, an independent ion source such as a corona offers several advantages for studying trace compounds present in the exhaust. First, the ion/neutral reaction time is typically constant and more easily estimated, which in turn allows absolute parent neutral concentrations to be more readily determined. Reaction times can also be varied in a stepwise manner without having to change the aircraft to apparatus distance. Ion lifetimes using an independent ion source are also typically shorter, thus minimizing measurement interferences for a wide range of potentially interesting products that would otherwise not form terminal ion species. An independent ion source could also be expected to provide a more stable and intense source of ions than a jet engine. An independent ion source operated at ambient pressure should thus be considered for the study of jet and rocket exhaust.

In addition to potential fluctuations in ion concentrations, neutral concentrations being observed in jet exhaust using the corona source also varied dramatically in time because of crosswinds. As would be expected, these fluctuations were most common at the largest engine-to-

apparatus distances. Fortunately, our measurements were not the only ones being performed. Phillips Laboratory had a neutral mass spectrometer instrument, which measured a number of different compounds present in the jet exhaust located immediately forward of the previously discussed instrument. Some of these compounds were known to be in the exhaust and were at relatively high concentrations. The measurement of these compounds thus provides a good tracer for determining the extent to which the two instruments were within the jet exhaust plume. However, the measurement results from the two different instruments have not as yet been combined. Thus, the concentration of any specific ions in the spectra shown in the following Figures should be considered tentative until the effect of winds are included in the data analysis.

Ion Measurements

The first measurement performed behind a jet engine was a nine-minute long observation of positive ions produced only by the jet engine. This measurement was made at a distance of about 170 feet from the engine under reasonably windy conditions.

Since jet engines were not expected to bathe the two instruments in a uniform concentration of exhaust or to be operated for a known amount of time, it was decided that several short integration time spectra should be measured as opposed to one long integration time spectrum in the hope that at least some time would be spent looking at each mass when the exhaust was reaching the instrument. Even if all of the spectra are summed, less than two seconds of integration time was available per mass for the 290 masses which were measured. However, two seconds per mass turned out not to be a sufficient integration time; hence, no peaks were seen above the background count rate in the July 27 measurement. At this point, it was decided that a corona ion source would be installed at the entrance to the sampling tube to produce sufficiently high ion concentrations allowing rapid measurements of ion spectra to be made. Figure 1a shows a typical positive mass spectrum measured on July 28 with the engine running at about 170 feet in front of the ion sampling instrument. (Typical in this case means that the deflection of jet exhaust away from the measurement apparatus by wind was thought to be minimal. All of the present data

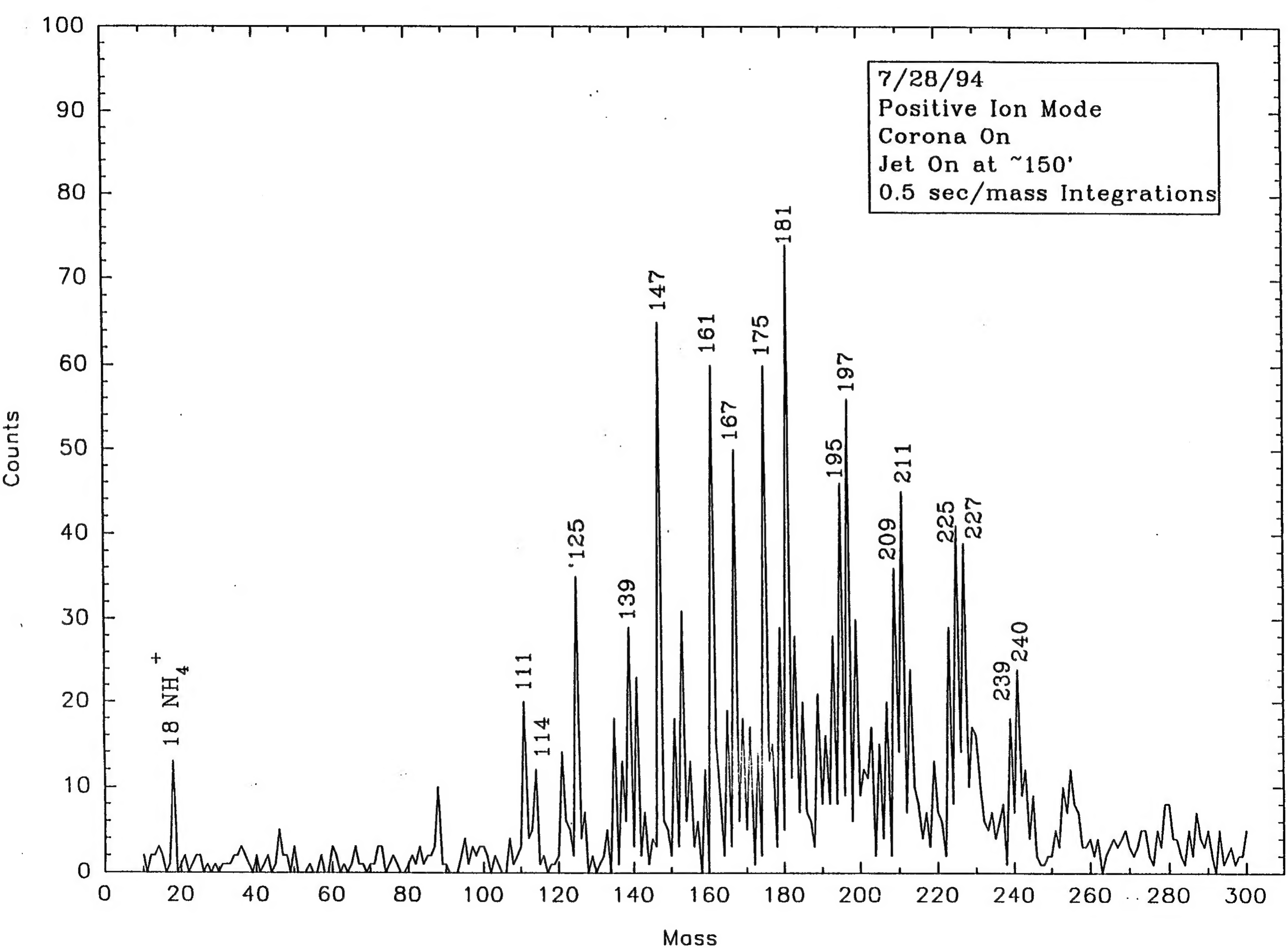

7/28/94
Positive Ion Mode
Corona On
Jet On at ~150'
0.5 sec/mass Integrations
Counts
Mass
18 NH4+
111
114
'125
139
147
161
167
175
181
195
197
209
211
225
227
239
240

FIGURE 1a

are available as a function of measurement time, and a merging of the Phillips Lab and Georgia Tech data would provide improved insight into the origin of each spectral component.) The total ion/neutral reaction time is estimated to be about 0.2 seconds with a terminal ion concentration on the order of 10^6 ions/cm^3. Figure 1b shows the average of several spectra measured in the same manner as those in Figure 1a, but without the jet engine operating. Clearly, these two spectra are dramatically different. The natural or background spectra (Figure 1b) is dominated largely by what appear to be ammonium ions seen at masses 18 and 36 (NH_4^+ and $NH_4^+ \cdot H_2O$ respectively). The peak at mass 37 is thought to be $H_3O^+ \cdot H_2O$, and no identity is presently suggested for the remaining peaks . In Figure 1a, a small ammonium ion peak remains, but at only about 1% of its original magnitude. The majority of the ammonium ions that are present in ambient air have apparently been replaced by a wide range of different compounds in the jet engine exhaust. It is likely that essentially all of the new peaks correspond to compounds with higher proton affinities than ammonia. It is also likely that many of them are some type of hydrocarbons. The 14 amu periodicity seen for many of the larger peaks is suggestive of successively higher numbers of CH_2 groups. At this time, no specific chemical identifications can be offered for the higher mass peaks. Figure 2a shows a negative ion spectrum measured on July 28 in the same manner as the positive spectrum in Figure 1a, with the exception that the jet engine was only 100 feet from the measurement instrument in Figure 2a. Figure 2b shows the natural or background spectrum under the same conditions. The background ion spectrum appears to be made up largely of NO_3^- core ions seen at masses 62 and 125 (NO_3^- and $NO_3^- \cdot HNO_3$ respectively) with an additional large peak at mass 103 which is probably $C_3H_3O_4^-$. Note that there is a peak at mass 97, but that it is far from the largest in the spectrum. Alternatively, the mass 97 peak in Figure 2a is the largest peak, and in all likelihood corresponds to $H^{32}SO_4^-$. The related $H^{34}SO_4^-$ isotopic peak is also seen at mass 99 in the proper ratio, helping to confirm the identity of both peaks. The mass 125 peak remains present in both engine exhaust and background spectra. In previous atmospheric studies, two sulfur-related negative ion peaks measured at masses 142 and 158 were determined to be NSO_6^- and NSO_7^-, respectively. It is possible, but not at all certain, that the present peaks at

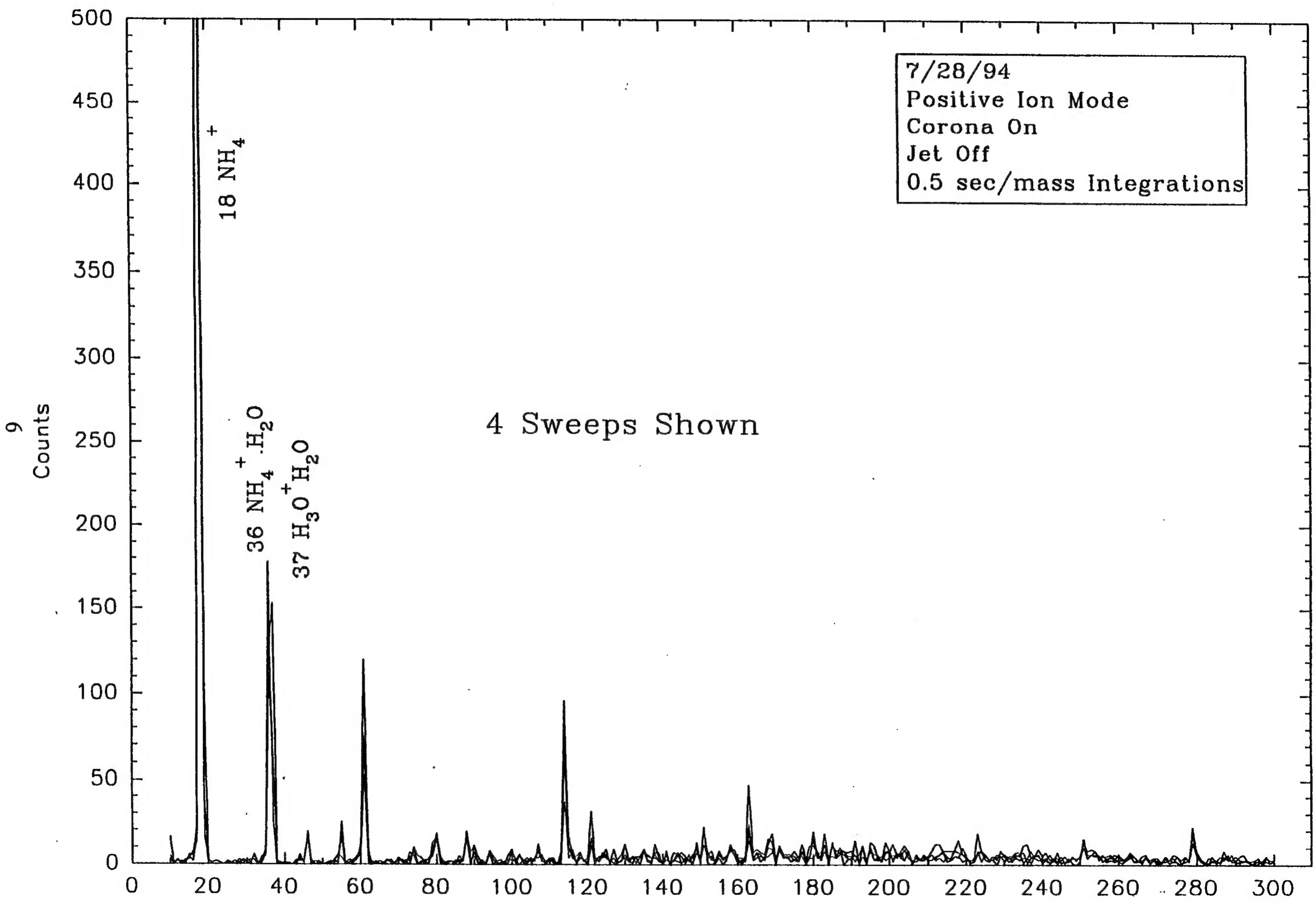
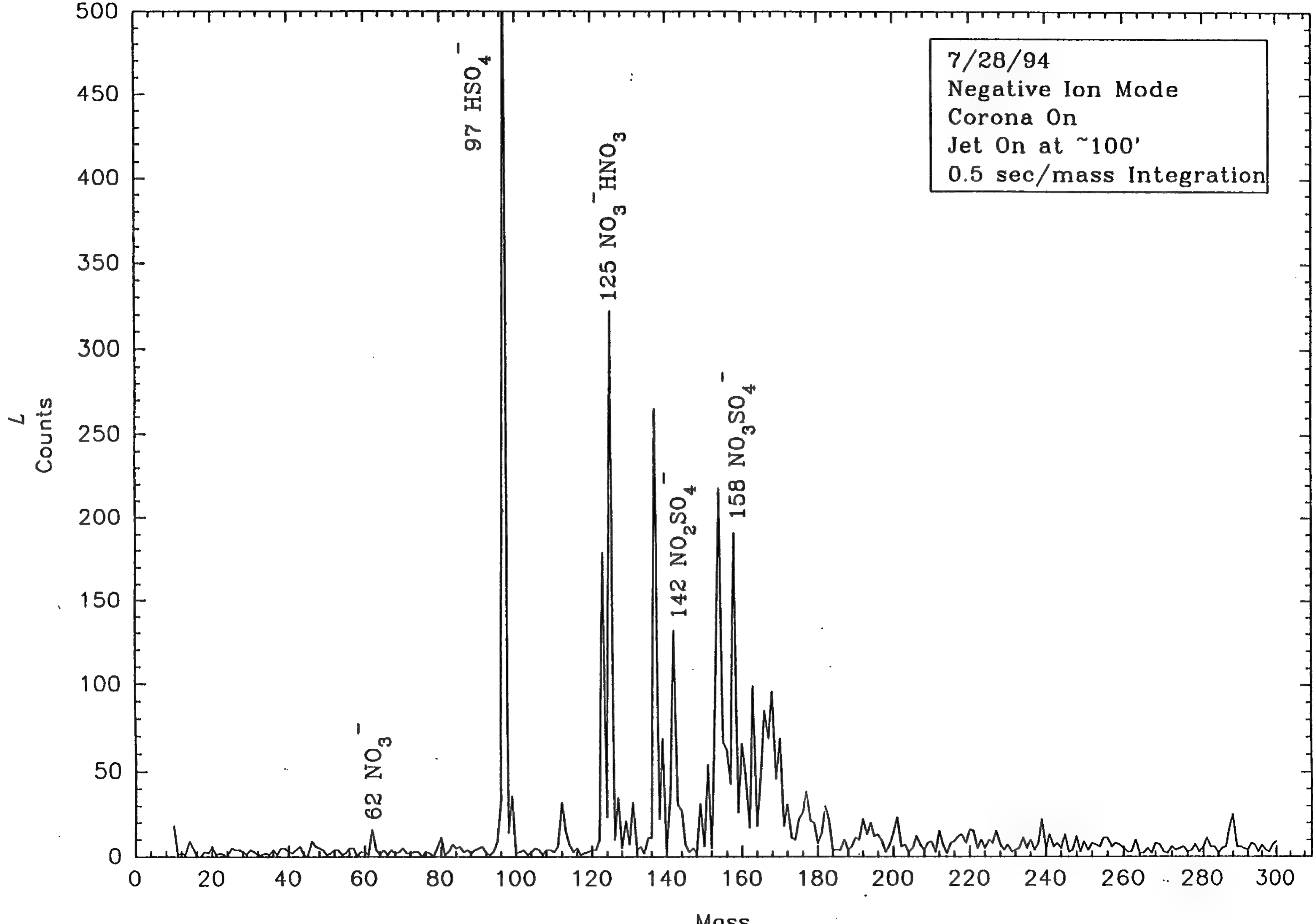
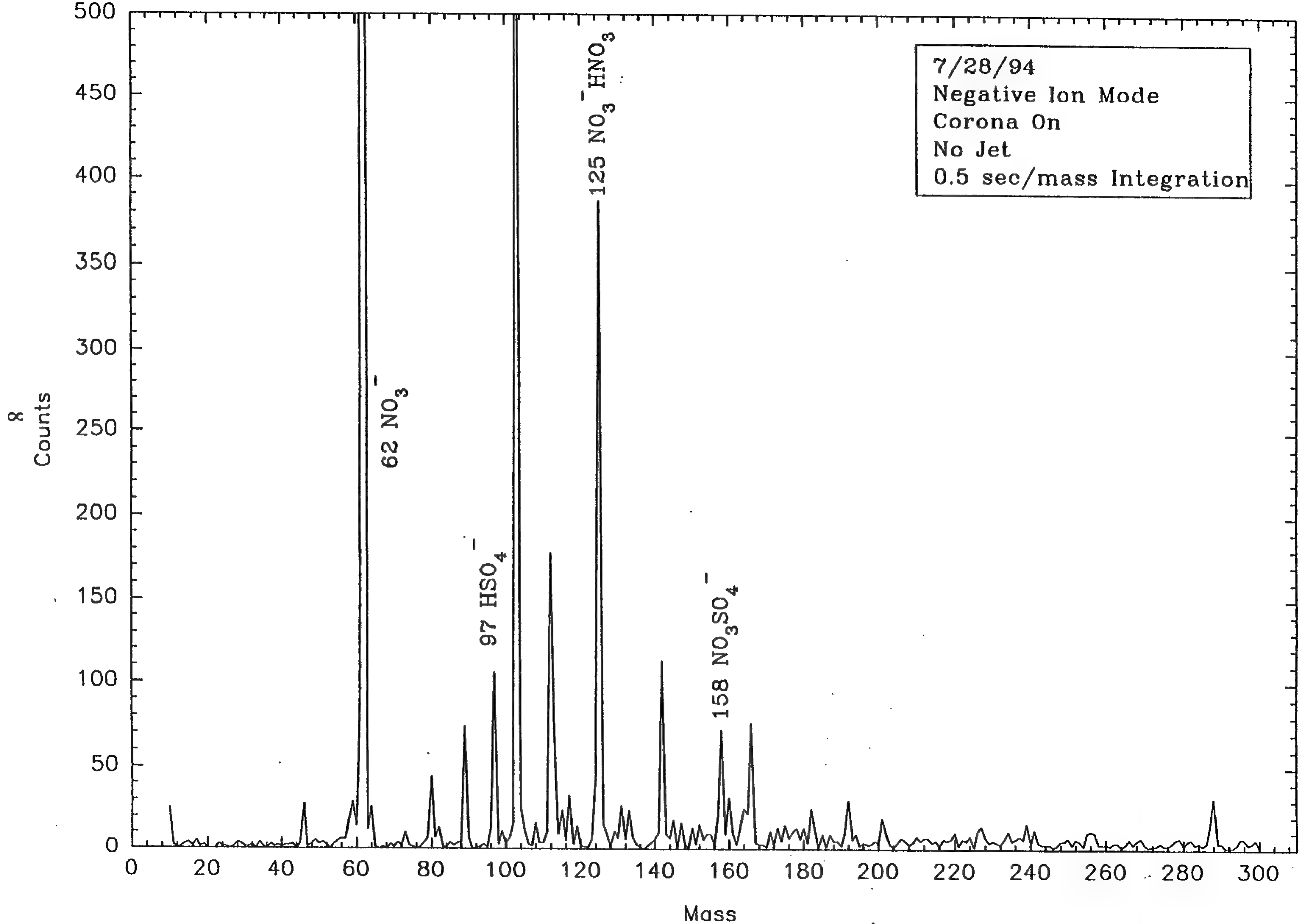

7/28/94
Positive Ion Mode
Corona On
Jet Off
0.5 sec/mass Integrations
4 Sweeps Shown
18 NH_4^+
36 $NH_4^+ \cdot H_2O$
37 $H_3O^+H_2O$
Counts
Mass
0
50
100
150
200
250
300
350
400
450
500
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

FIGURE 1b



7/28/94
Negative Ion Mode
Corona On
Jet On at ~100'
0.5 sec/mass Integration
62 NO_3^-
97 HSO_4^-
125 $NO_3^- HNO_3$
142 $NO_2SO_4^-$
158 $NO_3SO_4^-$
Counts
Mass

FIGURE 2a



7/28/94
Negative Ion Mode
Corona On
No Jet
0.5 sec/mass Integration
62 NO_3^-
97 HSO_4^-
125 $NO_3^- HNO_3$
158 $NO_3SO_4^-$
Counts
Mass

FIGURE 2b

masses 142 and 158 correspond to these same compounds. No chemical identifications are presently offered for the remaining ion peaks.

Figure 3a shows a positive spectrum measured on the morning of July 29. Ions were again produced by a corona source, but this time the jet engine was only 75 feet in front of the ion measurement instrument. Also, the energy available to dissociate clustered ions before they were mass analyzed was doubled for this one measurement (the collisional dissociation chamber was operated at 60 volts as opposed to 30 volts). The other four sets of measurements were all made at a lower collision energy which typically removes only H_2O molecules from the ions entering the chamber. The higher collision energy used for the spectra shown in Figures 3a and b helped ensure that all weakly bound clusters were removed from the already complex positive ion spectra, particularly in the higher mass range. Figure 3b shows a background ion spectrum with the jet exhaust absent. A comparison between Figures 1a and 3a shows that most of the major peaks are the same at the two different collision energies, suggesting that these peaks correspond to stable core ions. Figures 4a and b show the negative ion spectrum measured at 75 feet behind the jet engine and a background spectrum, respectively. Sulfuric acid clearly dominates the spectrum shown in Figure 4a with peaks at mass 97, 195, and 293 (HSO_4^-, $HSO_4^- \cdot H_2SO_4$, $HSO_4^- \cdot (H_2SO_4)_2$). Also, the peak at mass 112 may well be SO_5^-. Why the H_2SO_4 concentration appears to be so much higher in Figure 4a compared to Figure 2a is unclear, but the possible effects of winds and dilution need to be considered before any importance is placed on this difference.

In addition to the measurements made with the corona source turned on, several attempts were made to measure ion spectra with the corona source turned off. The corona source was turned off while the jet engines were still operating but just after the spectra in Figures 2a, 3a, and 4a were measured. None of these spectra showed any discernible peaks except after Figure 4a, and this spectrum is shown in Figure 5. It should be noted, however, that there is only one peak in Figure 5 at mass 195, and that this peak corresponds to only a single measurement at that mass. Thus, while a large peak at mass 195 might be expected from the observation in Figure 4a, its

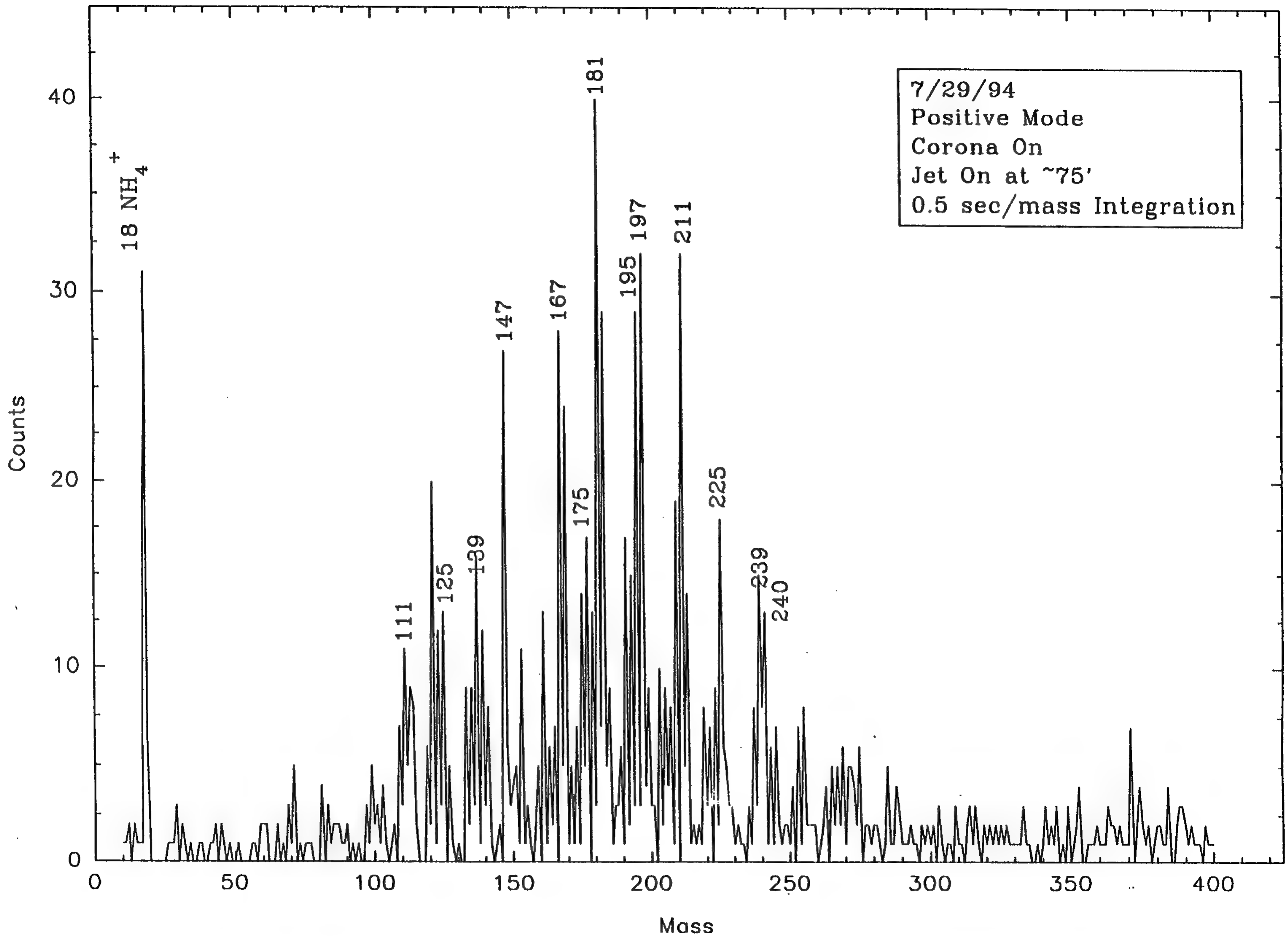

7/29/94
Positive Mode
Corona On
Jet On at ~75'
0.5 sec/mass Integration
18 NH4+
111
125
139
147
167
175
181
195
197
211
225
239
240
Counts
Mass
0
10
20
30
40
0
50
100
150
200
250
300
350
400

FIGURE 3a

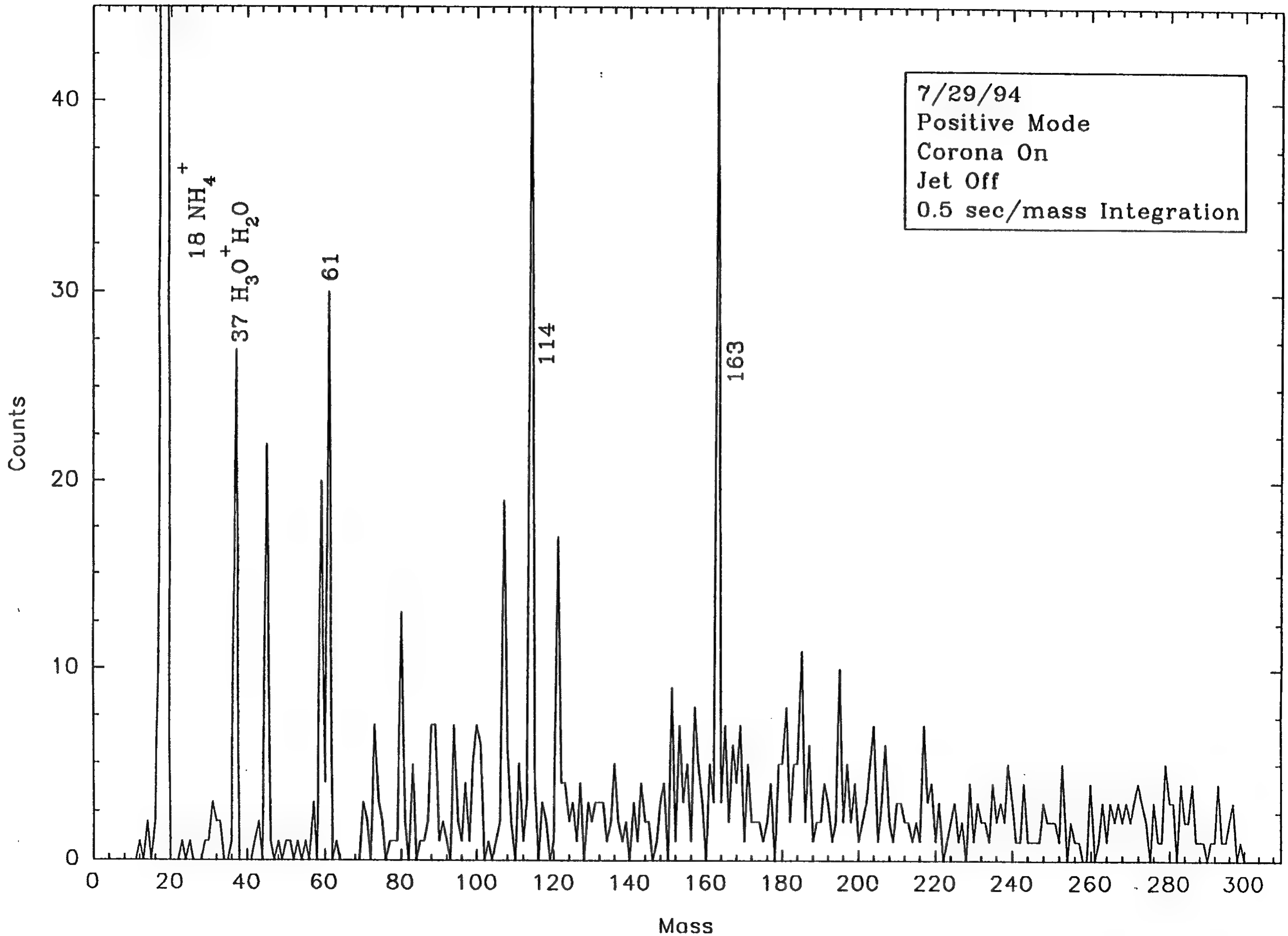
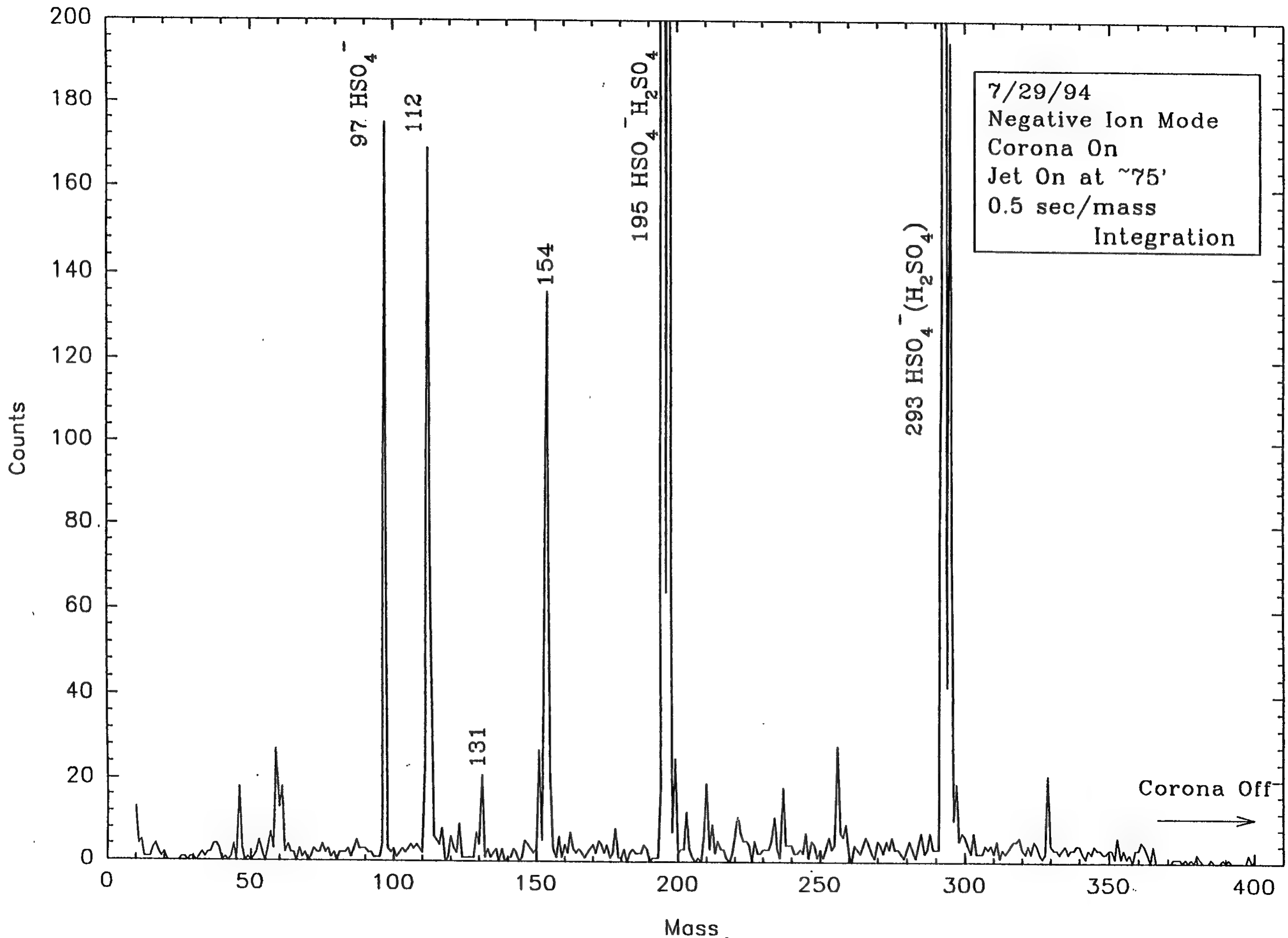

7/29/94
Positive Mode
Corona On
Jet Off
0.5 sec/mass Integration
18 NH_4^+
37 $H_3O^+H_2O$
61
114
163
Counts
Mass
0
10
20
30
40
0
20
40
60
80
100
120
140
160
180
200
220
240
260
280
300

FIGURE 3b


7/29/94
Negative Ion Mode
Corona On
Jet On at ~75'
0.5 sec/mass
Integration
97 HSO_4^-
112
131
154
195 $HSO_4^-H_2SO_4$
293 $HSO_4^-(H_2SO_4)$
Corona Off
Counts
Mass
0
20
40
60
80
100
120
140
160
180
200
0
50
100
150
200
250
300
350
400
FIGURE 4a

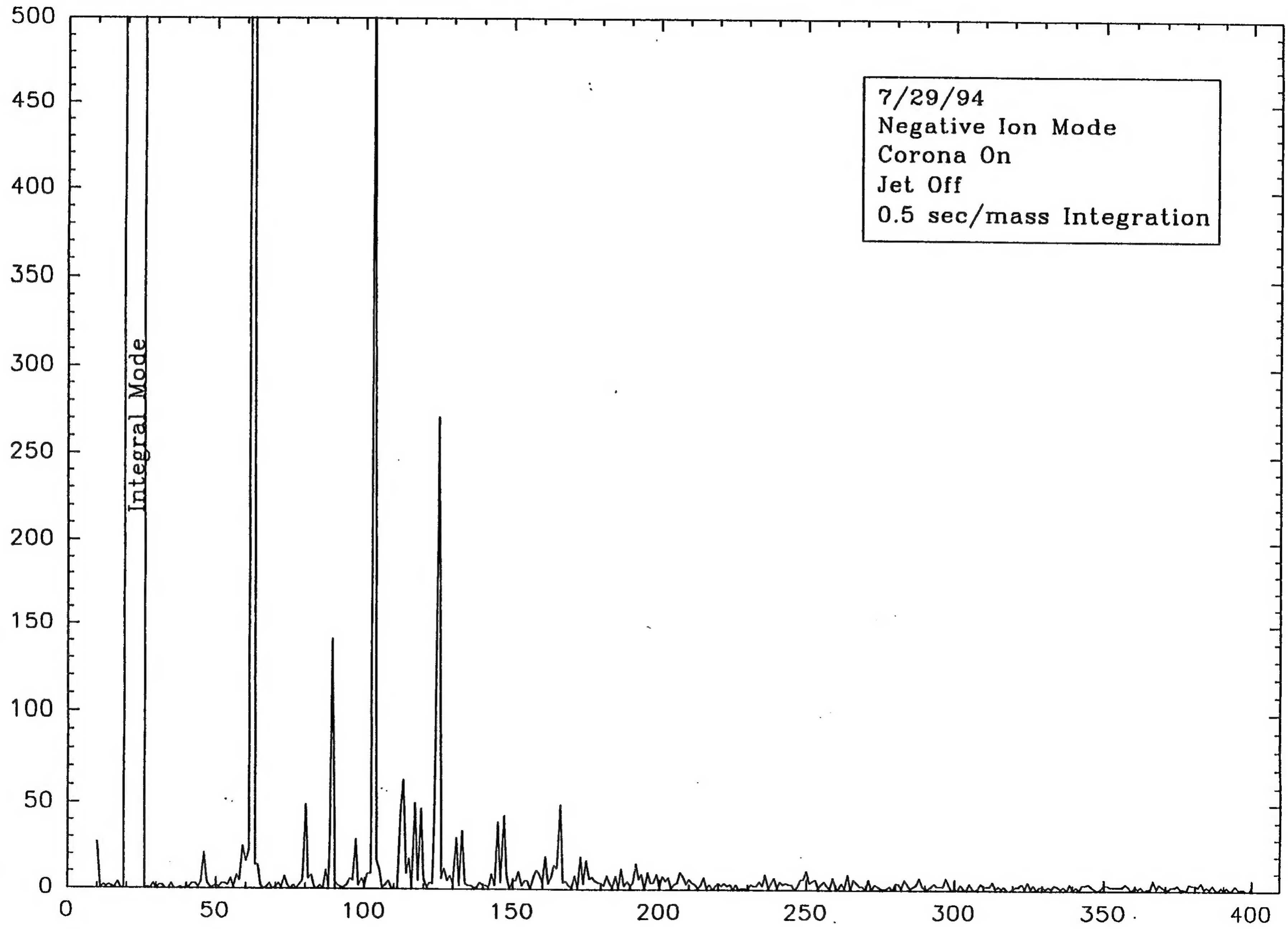

7/29/94
Negative Ion Mode
Corona On
Jet Off
0.5 sec/mass Integration
Integral Mode
Counts
Mass
0
50
100
150
200
250
300
350
400
450
500

FIGURE 4b

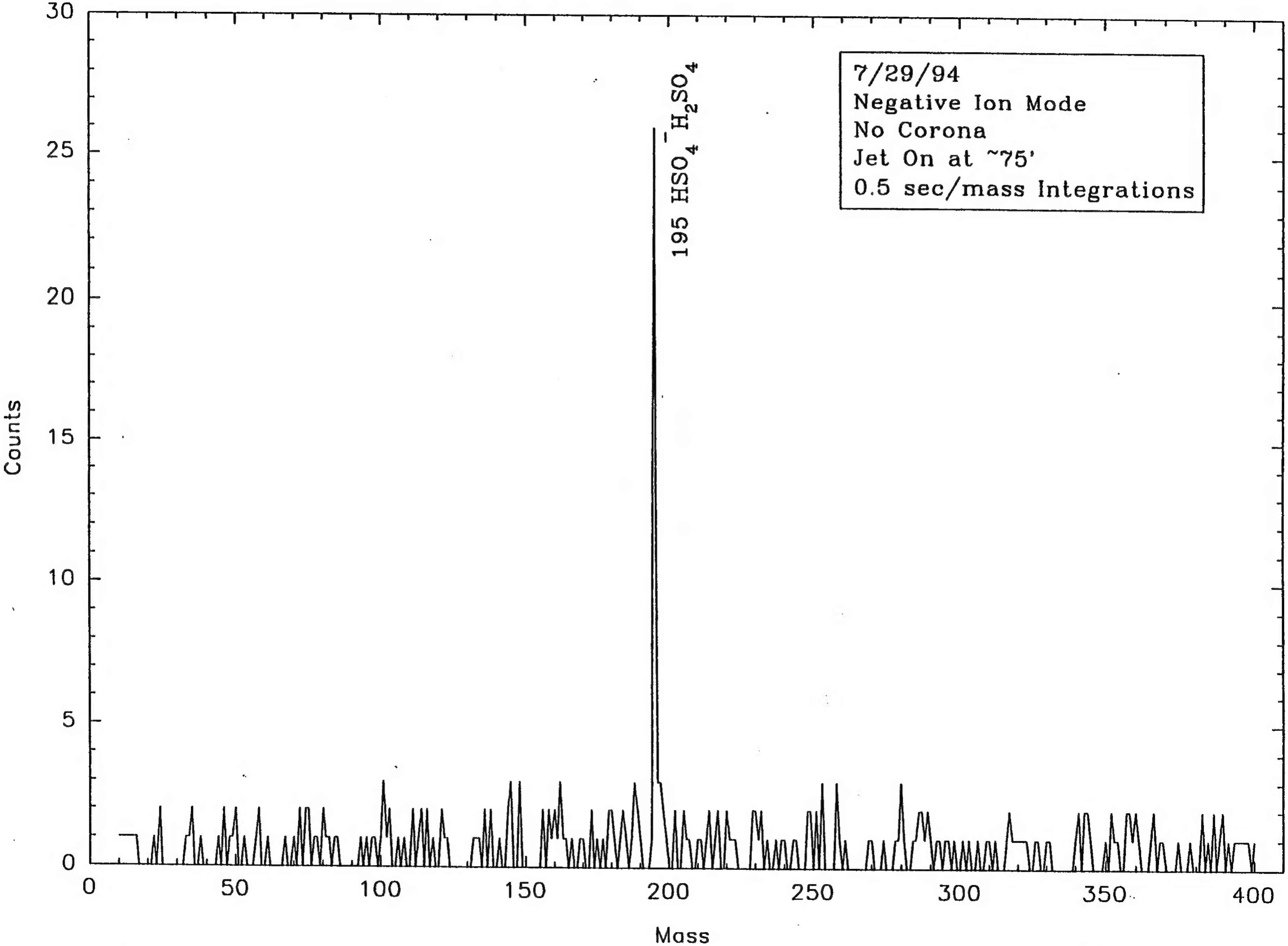

7/29/94
Negative Ion Mode
No Corona
Jet On at ~75'
0.5 sec/mass Integrations
195 $HSO_4^-H_2SO_4$
Counts
Mass
0
5
10
15
20
25
30
0
50
100
150
200
250
300
350
400

FIGURE 5

presence is still somewhat uncertain because of a lack of more than one data point. While no peaks were observed in the other non-corona spectra, the average of the overall count rate was measured during engine operation and compared to engine off periods. The result suggests between a zero to possibly a 10^3 ion/cm^3 enhancement in ion concentration in the jet exhaust compared to ambient air. This is in agreement with other observations and again emphasizes the need for an independent source of ions unless much longer integration times can be used.

Conclusions

The field study at Eglin AFB was very successful, particularly considering that it was the first time that this type of measurement was attempted. A substantial amount of data was obtained in both positive and negative ion spectra. Data were also obtained in both spectra for more than one engine test and engine distance so that intercomparisons can be made. The negative spectra tend to be far less complicated so that some immediate interpretations can be made, such as the identification of enhanced sulfuric acid concentrations in the jet exhaust. The positive spectra, on the other hand, only allow more general conclusions to be drawn, such as the probable presence of numerous high proton affinity hydrocarbons to the near exclusion of the ammonium ion. The positive spectrum will require laboratory studies of the ions produced in jet fuel vapor before a more complete interpretation can be provided. A study of these ions is planned as soon as this jet fuel is made available. The Eglin measurements also provide a great deal of new insight into how jet exhaust measurements can be improved in future studies. Included among these possible improvements are: the use of an ion source similar to that presently used to measure atmospheric H_2SO_4; the use of a much smaller sample inlet placed very close to the jet engine but off to the side of the exhaust stream; and, if possible, measurements made of exhaust from engines operating at full power.

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